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(54) Title: ANTI-WEAR ADDITIVES AND THEIR USE

(57) Abstract

A zinc-free anti-wear additive composition for an industrial fluid comprises as an active anti-wear ingredient at least one novel amine phosphate which is the reaction product of at least one n-heptyl acid phosphate with at least one aliphatic amine having at least 9 carbon atoms.

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ANTI-WEAR ADDITIVES AND THEIR USE

This invention relates to certain new materials capable of imparting anti-wear properties to industrial fluids such as hydraulic fluids and gear oils.

It is known that zinc-based additives can be included in industrial fluids such as gear oils to impart high performance wear resistance. However, it is desired to move away from the use of materials containing zinc which cause problems in use, such as hydrolytic stability, to additives which are zinc free and ashless. While certain phosphorus containing additives, such as tri-alkyl or tri-aryl phosphates, have been proposed for other purposes in industrial fluids, there has been nothing, in any way, to suggest their use as anti-wear additives which would be capable of matching or improving upon the performance of the presently employed zinc-based additives.

Accordingly, the present invention provides a zinc-free anti-wear additive composition for an industrial fluid comprising as an active anti-wear ingredient an amine phosphate which is the reaction product of at least one n-heptyl acid phosphate with at least one aliphatic amine having at least 9 carbon atoms, preferably at least 12 carbon atoms.

The n-heptyl acid phosphate may be the monoheptyl phosphate or diheptylphosphate or a mixture thereof, suitably a mixture of about 50% mono and 50% diheptyl phosphate.

The aliphatic amine preferably has at least 12 carbon atoms. The aliphatic moiety is preferably an alkyl, alkenyl or alkoxyalkyl group. The amine is preferably a p-amine. Suitable amines are the C_{12-14} alkylamine available commercially as "Primene 81R" from the Rohm and Haas Company

or the C_{18} alkenylamine of formula $H_2N(CH_2)_7 = (CH_2)_{11}$ available commercially as "Armeen O" from Akzo Chemie Nederland BV, or "Radiamine 6172" from Petrofina s.a., Belgium. Alternatively, an alkoxyalkylamine such as 3-isononyloxypropylamine (available from Hoechst AG) may be employed.

The amine phosphate active ingredients based on C_7 acid phosphates are new per se and are, therefore, included within the scope of the invention.

The additive composition of the invention can be employed in a variety of base fluids including conventional mineral based fluids, such as BP Virgin, or may also be used in natural or synthetic ester based fluids.

The concentration of the amine phosphate ingredient will be selected dependent on the base fluid chosen and the intended use of the fluid. It has been found that, for hydraulic use, using a mineral base fluid, a preferred concentration is at least about 0.05 and preferably at least 0.09 percent by weight, while for gear oil use, the preferred concentration of amine phosphate is at least about 0.09 and preferably at least 0.17 percent by weight. The upper limit of a satisfactory concentration range can be established dependent on economic considerations and required performance.

The additive composition may contain a wide variety of additives in addition to the amine phosphate. Thus, dependent on the end use, the composition may contain a polysulphide load carrying and anti-wear material. Other additives which may be used include dialkylhydrogen phosphite or tri-alkyl or tri-aryl phosphates (for the purpose of load carrying and anti-wear), copper passivators, such as alkyl dithiadiazoles and benzotriazole derivatives, alkyl p-amines (for the purpose of corrosion inhibition and anti-wear), antifoam

agents such as silicon based or non-silicon Mobilad C402 and anti-oxidants such as 2,6-di-tert-butyl-4-methyl phenol, Additin 10 from Rhein Chemie Rheinau GmbH and Irganox L57 from Ciba-Geigy Industrial Chemicals. The exact composition will depend on the intended use and nature of the base fluid.

The amine phosphate may be prepared by directly reacting the amine with the N-heptyl acid phosphate (preferably in substantially equimolar proportions), followed by cooling of the reaction mixture which is exothermic. The product is then incorporated with the other additive components to produce an additive composition for incorporation at appropriate concentration in the base fluid.

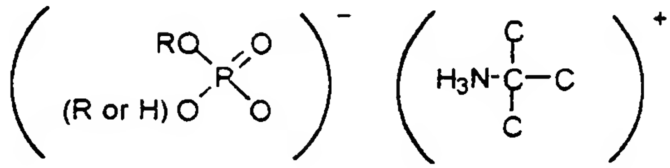
Alternatively, the amine phosphate may be prepared in situ by separately adding to a suitable diluent the acid phosphate and the amine and blending, suitably at elevated temperature, for example, about 60ºC before adding the remaining additives, thus avoiding any problems of exothermicity. The diluent may be the, or one or more of the, major components of the composition, suitably a polysulphide component but it will be appreciated that the diluent may be, for example, the ultimately intended base fluid, such as BP base fluid. Preferably the composition includes a dialkyl hydrogen phosphite which is suitably added after the other additives such as copper passivators, corrosion inhibitors, anit-foam agents and antioxidants.

The invention will now be illustrated with reference to the following examples.

Example 1 Preparation of $C_{12\text{-}14}$-amine n-heptyl phosphate

Projected

Formula:



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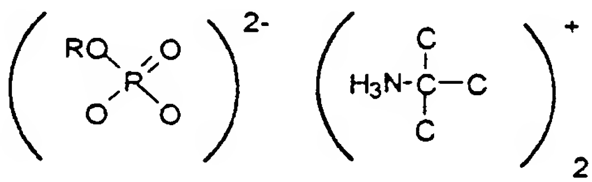

$R = C_7H_{14}$ $C = C_{12} - C_{14}$ range

Primene 81R (a $C_{12\text{-}14}$ amine available from Rohm and Haas) was added to a glass lined (or stainless steel) vessel. n-Heptyl acid phosphate (available from Albright and Wilson) or Elf Atochem was added slowly with stirring. The two reactants were employed in the ratio of 59.7% n-heptyl acid phospate to 40.3% Primene 81R.

The reaction was exothermic. Blending was continued for at least 30 minutes and the reaction mixture allowed to cool.

The resulting product was a light yellow liquid which was characterised by the infrared spectrum (measured by KBr disc) given in Figure 1 and the analytical data below:

Phosphorus	6.80 to 8.49%
Nitrogen	2.82 to 3.23%
Density (20°C)	0.96 g/ml approx.
Flash point (PMC)	92°C min.
Viscosity (100°C)	48 mm^2/sec (typical)

Exampl 2 Preparation of additive composition.

An additive composition suitable for use in a hydraulic fluid or gear oil was prepared by the following altemaitve methods:

A) To a warmed solution of polysulphide (TPS 32 available from Elf Atochem) to which was dissolved the antioxidant (Additin 10), there was added the n-heptyl amine phosphate prepared as described in Example 1 above and other additives as given below followed by blending for a minimum of 30 minutes and cooling.

B) Polysulphide and Additin 10 were added to a blend vessel to which was further added n-heptyl acid phosphate at 6.23% and Primene 81R at 4.20%. The reaction mixture was heated to a maximum temperature of 60°C and blending continued to homogeneity and until all the antioxidant (Additin 10) was dissolved. The remaining additives, as given below, were then added, blending continued for a minimum of 30 minutes and the mixture cooled.

The resulting additive composition can be used (depending on the application) as follows in terms of a percentage range (by weight):

	Range	Example
Polysulphide	50 to 75	61.35
Amine phospate	4 to 28	10.43
Dialkyl hydrogen phosphite	4 to 28	6.14
(e.g. dibutyl hydrogen phosphite)		
Copper passivator	6 to 17	3.68
(e.g. thiadiazole passivator)		
Alkyl p-amine	4 to 28	7.06
Anti-foam agent	0 to 1	0.30
(e.g. Mobilad C405)		

Antioxidants (e.g. phenolic/aminic mixture)	0 to 12	11.04

The additive composition was obtained in both methods as a yellow amber oily liquid, homogeneous, clear and bright. The infra red spectrum for the product from methods A) and B) is given in Figure 2.

The analytical data is:

Phosphorus	1.50 to 1.94%
Nitrogen	0.99 to 1.30%
Sulphur	17.2 to 23.3%
Density	0.98 g/ml (typical)
Flash Point (PMC)	50°C (min)
Viscosity 100/40°C	10/143c St

Example 3 Use of Additive Composition in Hydraulic Oils

The additive composition described in Example 2 above was blended into base fluids as given in Table 1 below to give two ISO VG 46 to 68 hydraulic oils and subjected to a series of standard tests as given in the Table. It is to be noted that the test results are of the level not normally expected for zinc free ashless compositions. The additive composition has provided a high standard hydraulic oil performance and, in particular, very low wear rates in the Vane pump test.

TABLE 1

Base Fluid	Test Ref.	Fluid 1 BP Virgin	Fluid 2 BP Virgin	Fluid 3 Re-refined mineral oil
Additive Comp		0.80 wt. %	0.80 wt. %	0.90 wt. %#
Viscosity cSt @ 40°C	IP 71	47.3	68	46
Steel Corrosion	IP 135	Pass A+B	Pass A+B	Pass A+B
Copper Corrosion	IP 154	1b	1b	1b
TOST (1000 hr,	DEF STAN			
MG koh/gm increase)	0550/57	1.20*	---	0.24
Foam 1 mls/mls @ sec	IP 146	0	0	0
2 "		20/0 @ 5	20/0 @ 3	20/0 @ 5
3 "			0	0
Timken O.K. Load (lb)	IP 240	50	---	---
FZG stage	CEC	pass 11,	---	pass 12
	L-07-A-85	fail 12		
Vane Pump	IP 218			
Ring wt. loss mg		5.1 (120 max)	---	21.7
Vane wt. loss mg		0.8 (30 max)	---	16.4
Wt. loss, mg/hr	IP 281	0.00236	---	0.15

* This formulation contained an additional 0.1% antioxidant

Additive composition of Example 2 plus additional 0.1% antioxidant.

Example 4 Use of Additive Composition in Gear Oils

The additive composition described in Example 2 above without antioxidants was blended into base fluids as given in Tables 2 and 3 below to give gear oils in the ISO 100 to ISO 320 range. The blends were subjected to a series of standard tests as given in the Tables.

TABLE 2

Test	Units	ISO VG.100	ISO VG.150	ISO VG.220	ISO VG.320
Rust Test, IP 135B (Based on 1.45% wt)		No Rust	-	-	No Rust
4 ball Wear Test, IP 239 1.45% wt					
1 hr, 20 kg, 1800 rpm;					
MWSD	mm	0.28	0.32	0.32	0.27
ISL	kg	130	120	160	110
Weld Point	kg	220	240	250	250
1.50% wt					
1 hr, 20 kg, 1800 rpm;					
MWSD	mm	0.35	0.30	-	-
ISL	kg	130	115	-	-
Weld Point	kg	240	240	-	-
1.55% wt					
1 hr, 20 kg, 1800 rpm;					
MWSD	kg	0.35	0.30	-	-
ISL	kg	140	140	-	-
Weld Point	kg	240	240	-	-

It will be seen from the above Table that there was provided satisfactory gear oil performance at an additive combination of 1.45% for ISO V.G. 150 and above and an additive treat rate of 1.50% for ISO V.G. 100.

TABLE 3

Test	Method	Units	Gear Oil V.G. 100 + 1.5% Additive Composition	V.G. Limits
Viscosity at 40°C	IP 71	cSt	103.0	9.50 - 105.0
Viscosity at 100°C	IP 71	cSt	11.3	-
Viscosity Index	IP 226	-	95	95 min
Air Release Value, 50°C	IP 313	mins	14.1	18 max
Foam Sequence 1:-	IP 146			
Tendency		mls	nil	75 max
Stability		mls	nil	Trace max
Flash Point, PMC	IP 34	°C	198	190 min
Sulphur content	ICP	%	1.24	-
Phosphorus content	ICP	%	0.03	-
Copper Corrosion	IP 154			
3 hrs at 120°C		-	1b	Class 3 max
Rust Test	IP 135B	-	No Rust	No Rust
Oxidation at 121°C	ASTM D2893			
Increase in Viscosity at 100°C		%	4.4	6 max
4 Ball Wear Test	IP 239			
1 hr, 20 kg 1800 rpm;				
MWSD		mm	0.35	0.35 max
ISL		kg	130	-
Weld Point		kg	250	250 min
FZG, Fail Stage	DIN 51354	-	> 12	12 min
Timken OK Load	IP 240	lbs	65	60 mins

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Exampl 5 Use of Modified Additive Compositions

Further test fluids were prepared containing additive compositions prepared using the methods described in Examples 1 and 2 and using two alternative amine phosphates (one prepared using ARMEEN O and one prepared using iso-nonyloxypropylamine) and polysulphide and/or dialkyl phosphite additives in an amount of 1.0%/0.09 and 0.1%. The compositions were tested for anti-wear performance in accordance with IP 239. The compositions and results are given in Table 3 below. The base fluid was B.P. 150 Solvent neutral.

TABLE 4

	1	2	3	4	5	6	7	8	9
1) n-heptylacid phosphate + isononyloxy-propylamine (WT.%)	-	-	-	-	-	-	0.17	0.17	0.17
2) n-heptylacid phospate + PRIMENE 81R (wt.%)	0.17	0.17	-	-	0.17	-	-	-	-
3) n-heptylacid phosphate + ARMEEN O (wt.%)		-	0.17	0.17	-	-	-	-	-
polysulphide (wt.%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
phosphite (wt.%)	0.1	0.09	0.1	0.09	-	-	-	0.10	0.09
mean wear scar diameter (mm)	0.324	0.292	0.326	0.320	0.324	0.310	0.323	0.338	0.323

It can be seen from the above results that the preparation in Example 1, together with a dialkyl hydrogen phosphite and an amine phospate prepared using ARMEEN O and isononyloxypropylamine produce low anti-wear performance in the IP 239 Shell 4-ball test.

Example 6 Use of Additive Composition in Synthetic Ester Hydraulic Fluids

The additive composition described in Example 2 above was blended into synthetic ester base fluids of the grades given in Table 5 below and subjected to a series of standard tests as given in the Table.

TABLE 5

Grade HE	32	46	68	Limits
ISO Viscosity Grade VG	32	46	68	32/46/68
Pour Point, °C max	- 57	-51	- 51	-18/-15/-12
Steel Corrosion, max (DIN 51585)	Pass	Pass	Pass	Class 0-Method A
Copper Corrosion max (DIN 51759)	1b	1b	1b	Class 2-3 hours at 100°C
Air Release 50°C mins, max (DIN 51381)	<0.5	<0.5	1.7	5/10/10
Demulsibility, 54°C, mins, max (DIN 51549)	10	30	45	40/40/60
FZG, A8.3/90: Load Stage Fail, min	>12	>12	>12	10
Vane Pump Wear, mg, max (DIN 51389/2)		(1)		
Ring} @ 250 hours (1)		2.5	<120	120
Vanes		7.1	<30	30

Baader 95°C @ 3 days (DIN 51554/3) Viscosity change @ 40°C,% max mg KOH/gm change, max	(2) 0.7 -0.15	(2) -0.6 0.07	(2) 2.7 -0.08	(2) +20 +0.08
SRE-NBR 1 - seals (DIN 3538/1) Volume change, % max Hardness change, max	 10 -9.7	 10 -9.6	 10 -9.4	 -3/+10 ± 10
Foam Volume, ml/ml @ sec. max (DIN 51566) at 20°C at 95°C at 25°C (after 95°C)	 60/0@35 0 60/0@29	 0 0 0	 0 40/0@120 0	 150/0@120 75/0@120 150/0@120
Neutralisation Number mgKOH/gm (DIN 51558/1)	0.34	0.38	0.37	
Brugger, N/mm^2, min	43.8	45	>30	30
Biodegradability (CECL33T82), % min	>95	>95	>85	70
Viscosity Index	151	172	184	-
Copper Corrosion (DIN 51759A) @ 125°C, max	1b	1b	1b	Class 1
Steel Corrosion (DIN 51585B)	Pass	Pass	Pass	Pass
4-Ball (ASTM D2783) Weld Point, kg Load wear index, kg 1 hr wear @ 30 kg, MWSD, mm	200 >45 >0.35	200 52 0.330	240 49.5 0.360	- 45 -
Seal Tests @ 168 hrs (i) Medium NBR @ 80°C Volume Change, % Hardness Change (ii) Flurocarbon @100°C Volume Change, % Hardness Change (iii) Polyurethane @ 80°C Volume Change, % Hardness Change	 6.6 -7.3 1.3 -1.7 8.2 -10	 6.4 -7.0 1.5 -2 8.0 -9.0	 6.0 -6.9 1.2 -2 7.9 -9.5	 -3/+10 -10/+10 -3/+10 -10/+10 -3/+10 -10/+10

Stear stability %, max (DIN 51382) 100°C 250 cycles, loss	-	-4.3	-	± 10
(1) DIN 51389/2 @ 250 hours (2) Replaces DIN 51587 used for mineral oil based fluids.				

It will be seen from Table 5 that the fluids meet the Baader oxidation test requirement for synthetic ester base fluid hydraulic lubricants with very low viscosity and acid number increase after test. They meet the following lubricant specifications where the oxidation testing used was that developed for ester base fluids.

- DIN 51524, part 2
- SEB 181 - 222
- Ford U.MC 006-8004
- Brugger

The lubricants have been found to provide excellent corrosion protection, extreme pressure and anti-wear with a passing result in the Vickers 104C 250 hour vane pump test and very high FZG load stage performance. They are compatible with nitrile, fluorocarbon and polyurethane sealing material and their high viscosity index, low pour point and good filtration ensures that the lubricant properties are excellent.

It has been found that, when used with the applicants' water based metalworking fluids the lubricants show excellent separation properties. Their biodegradability of greater than 95% for the ISO VG 32 and 46 grade and greater than 85% for the ISO VG grade by CEC L33 T82 minimises their impact on the environment as do the properties of being heavy metal, chlorine free and ashless.

<u>Example 7</u> Use of Additive Composition in Synthetic Ester Gear Oil

The additive composition described in Example 2 above was blended into synthetic ester base fluids of the grades given in Table 6 below and subjected to a series of standard tests as given in the Table.

TABLE 6

Grade CLP	46	68	100	150	220	Limits 46/68/ 100/150/ 220
ISO Viscosity Grade VG	46	68	100	150	220	DIN 515550+ 51562/1
Pour Point, °C, max (ISO 3016)	-33	-27	-27	-27	-27	-15/-15/-12/-9/6
Copper Corrosion (DIN 51759)	1b	1b	1b	1b	1b	
Steel Corrosion, max (DIN 51355A)	Pass	Pass	Pass	Pass	Pass	Class O
Ageing, Behaviour (DIN 51586)						
Viscosity Increase @ 100°C max	<6	5.6	<6	<6	<5.7	6
Precipation Number ml max	<0.1	<0.1	<,0.1	<0.1	<0.1	0.1
FZG A8.3/90: Load Stage Fail min	>12	>12	>12	>12	>12	12
Weight loss mg/kwh max	0.028	<0.3	<0.3	0.006	<0.3	0.3
SRE-NBR 1 - seals (DIN 53538/3)						
Volume change, %	8.7	8.9	<8.9	<8.9	7.8	
Hardness change	-6	-5	<-5	<-5	-4	
Brugger, N/mm^2, min	56.1	51.9	>50	>50	66.6	50
Biodegradability, % (CE 33T82) max	>95	>95	>90	>85	>85	70
Timkin OK Load, lbs, min (ASTM D2783)	>60	85	>60	>60	>90	60

TABLE 6 - Continued

4-ball (ASTM D 2783) Weld Point, kg, min Load Wear Index min 1 hr Wear @ 20kg MWSD, mm, max (ASTM D2266)	 260 61.8 -	 280 61.9 0.304	 >250 >45 <0.35	 >250 >45 <0.35	 260 60.6 0.282	 250 45 0.35
Steel Corrosion (ASTM D665B)	Pass	Pass	Pass	Pass	Pass	Pass
Foam Suppression, ml/ml @ sec, max (ASTM D896) (1) (2) (3)	0 70/0 @ 19 70/0 @ 12 0	0 70/0 @ 34 10/0 @ 4	- - -	- - -	0 20/0 @ 120 20/0 @ 6	75/0 @ 120 75/0 @ 120 75/0 @ 120
Viscosity Index	187	184	>184	>184	194	-
Copper Corrosion (DIN 51759) @ 125°C max	1b	1b	1b	1b	1b	Class 2
Timkin Weight Loss, mg, max 25 lbs 30 lbs 35 lbs 40 lbs	 0.3 - - -	 - 0.5 - -	 - - - 0	 - - 0 -	 - - - 0.4	 6 6 6 6
Air Release 50°C max (DIN 51381	3.9	4.1	-	-	21.7	10/10/20 30/30
Demulsification 54°C min (DIN51599) max	23	28	<25 @ 82°C	<25 @ 82°C	25 @ 82°C	40/60/60 /-/-
Seal Tests @ 168 hrs max (i) Medium NBR @ 80°C Volume change % Hard Change	 -1.9 1	 -1.4 2	 - -	 - -	 -0.8 4	 +3/+10 -10/+10
(ii) Flurocarbon @ 100°C Volume Change % Hardness Change	 -0.9 -2	 0.2 -1	 - -	 - -	 0 0	 +3/+10 -10/+10

(iii) Polyurethane @ 80°C Volume Change % Hardness Change	 0.2 0	 0.6 -1	 - -	 - -	 0 -1	 +3/+10 -10/+10
Stear stability %, max (CEC-4-45-T-93/A) 100°C loss	<10	<10	<10	<10	-8.7	± 10

It will be seen from Table 6 that the lubricants meet the following internationally recognised specifications that were originally designed for mineral oil based fluids.

- DIN 51517, part 3
- SEB 181 -222
- Ford U-MC 002-8008
- U.S. Steel 224
- Brugger

We have found that the lubricants provide excellent corrosion protection, extreme pressure and anti-wear performance with an FZG load stage pass greater than 12. They are compatible with nitrile, fluorocarbon and polyurethane sealing material and their high viscosity index, low pour point and good filtration ensures that their lubrication properties are excellent.

Biodegradability of greater than 85% for the 220 grade and greater than 95% for the lower viscosity lubricants minimises the impact on the environment as does the properties of being heavy metal, chlorine free and ashless.

CLAIMS

1. An amine phosphate which is the reaction product of at least one n-heptyl acid phosphate with at least one aliphatic amine having at least 9 carbon atoms.

2. An amine phosphate according to claim 1 wherein the aliphatic amine has at least 12 carbon atoms.

3. An amine phosphate according to claim 2 wherein the amine is a p-amine.

4. An amine phosphate according to claim 3 wherein the amine is a C_{12-14} alkylamine, a C_{18} alkenylamine, or an alkoxylalkylamine.

5. A zinc-free anti-wear additive composition for an industrial fluid comprising as an active anti-wear ingredient at least one amine phosphate according to any one of the preceding claims.

6. An additive composition according to claim 5 wherein the amine phosphate component is present as a monoheptyl phoshpate or a di-heptylphosphate or a mixture thereof.

7. An additive composition according to claim 5 or 6 further comprising additives selected from polysulphides, dialkylhydrogen phosphites, tri-alkyl phosphates, tri-aryl phosphates, alkyl dithiadiazoles, benzotriazoles, alkyl p-amines, antifoam agents and anti-oxidants.

8. An additive composition according to claim 5, 6 or 7 in which the amine phosphate component has been prepared in situ by separately

adding to a suitable diluent the acid phosphate and the amine and blending before adding the remaining additives.

9. An additive composition according to claim 8 including a dialkyl hydrogen phosphite which has been added after addition of other additives.

10. An industrial fluid comprising a mineral base oil or a natural or synthetic ester base fluid incorporating an additive composition according to any one of claims 6 to 9.

11. An industrial fluid intended for hydraulic use wherein the amine phosphate component of the additive composition is present in an amount of from about 0.05 to about 0.09 weight per cent.

12. An industrial fluid intended for gear oil use wherein the amine phosphate component of the additive composition is present in an amount of from about 0.09 to about 0.17 weight percent.

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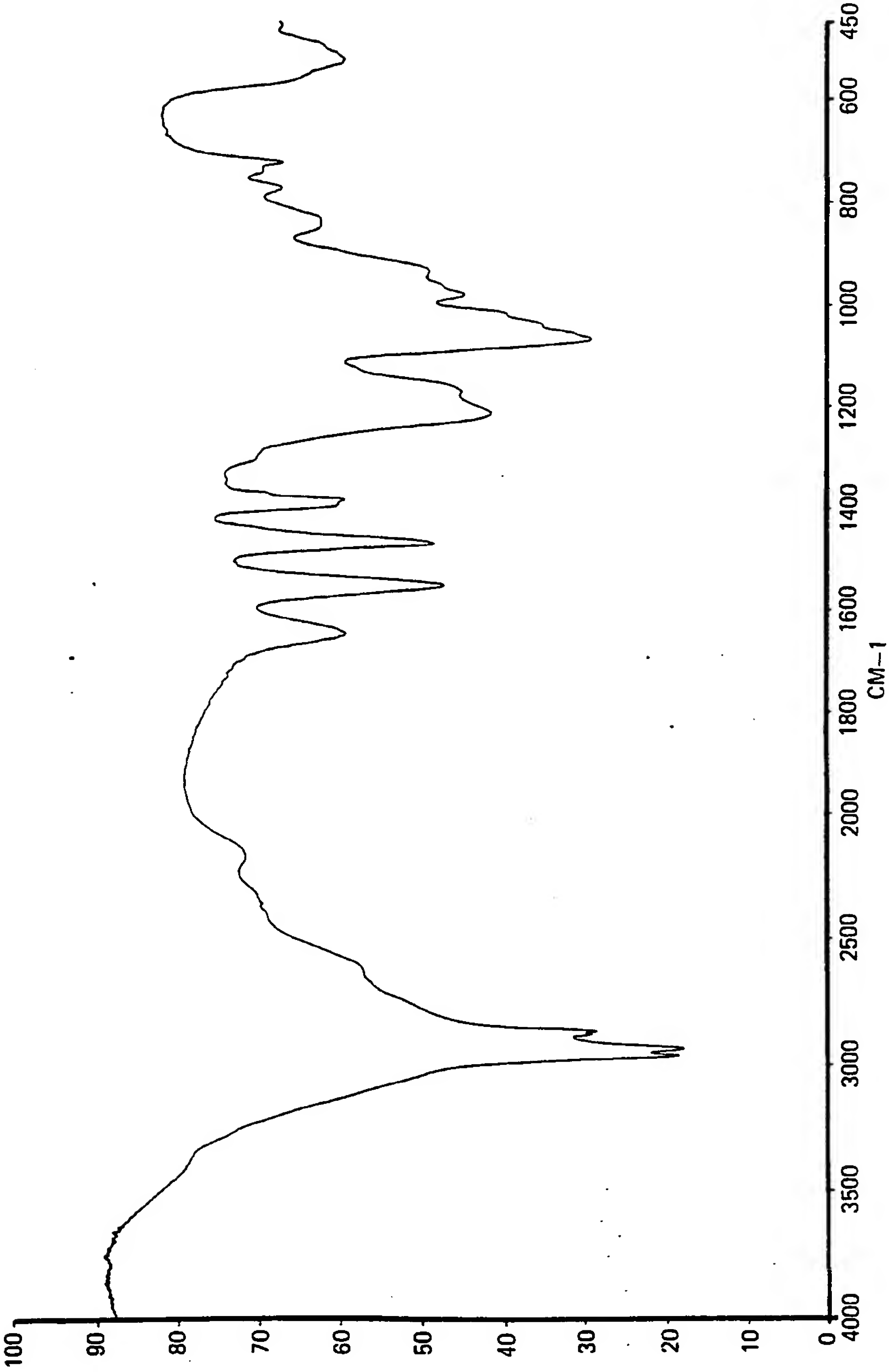

FIG. 1

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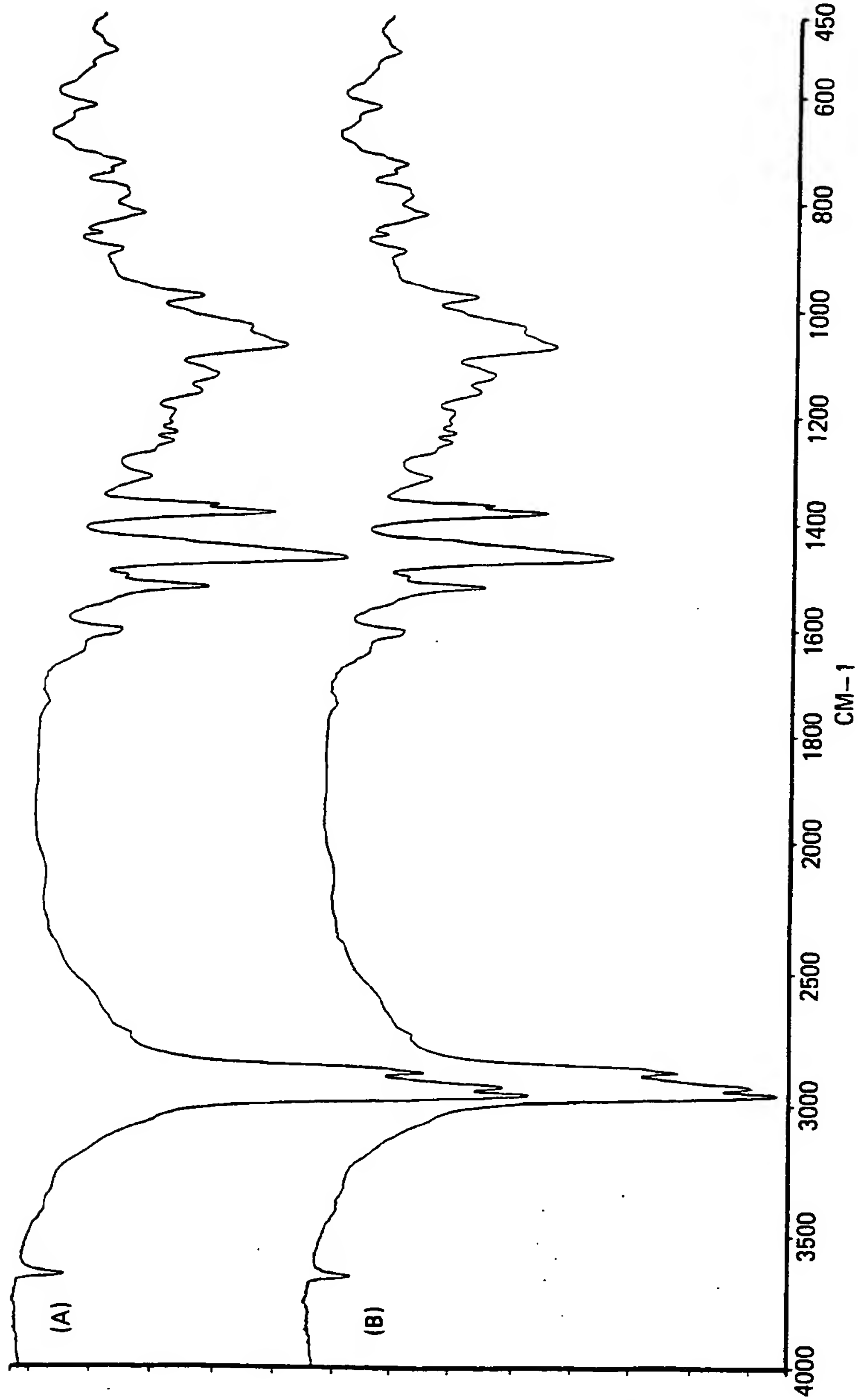

FIG. 2

BNSDOCID: <WO___9520592A1_I_>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/00148

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F9/09 C07F9/22 C10M137/08 C10M141/10
//(C10M141/10,133:06,133:44,135:20,137:02,137:04,137:08),
C10N30:06,C10N40:04,C10N40:08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 460 317 (ETHYL PETROLEUM ADDITIVES) 11 December 1991 see page 2, line 10 - line 14 see page 2, line 30 - line 31 see page 4, line 12 - page 5, line 16 ---	1-7
X	US,A,3 425 815 (R.H. ROSENWALD) 4 February 1969 see column 2, line 38 - line 42 see column 3, line 5 - line 7 see column 3, line 25 see column 4, line 11 - line 12 ---	1-6
A	WO,A,87 07637 (THE LUBRIZOL CORPORATION) 17 December 1987 see page 16, paragraph 1 -paragraph 2 see page 25, line 3 - line 11 --- -/--	1-5,7-12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
27 April 1995	11.05.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hilgenga, K

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Intern· al Application No
PCT/GB 95/00148

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO,A,95 06094 (EXXON RESEARCH AND ENGINEERING COMPANY) 2 March 1995 see claims 1,6,7,9 -----	1-5,7,8, 10-12

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		DE-A- 1545508	14-01-71
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		DE-T- 3789382	20-10-94
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		ZA-A- 8704205	15-12-87
WO-A-9506094	02-03-95	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)

BNSDOCID: <WO___9520592A1_I_>